12th International Conference on Fracture Mechanics of Concrete and Concrete Structures
FraMCoS-12
B.L.A. Pichler, Ch. Hellmich, P. Preinstorfer (Eds)

https://doi.org/10.21012/FC12.1282
MS15-1:2

MECHANICAL BEHAVIOUR AND 3D FRACTURE MORPHOLOGY OF SUSTAINABLE ENGINEERED CEMENTITIOUS COMPOSITES MODIFIED WITH BORON NITRIDE NANOPARTICLES

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Key words: Engineered Cementitious Composites, Nanoparticles, Fractal Analysis, Cracking Characteristics

Abstract: In the 21st century, humanity faces increasing concerns about climate change and natural hazards such as earthquake earthquakes and floods that induce deaths, homelessness and economic loss due to poor performance of civil infrastructure, particularly in ODA-eligible countries like Turkey, where the majority of infrastructures are mainly made of concrete. Therefore, it is also very important to ensure infrastructural assets are free from structural damage and are made up of environmentally friendly materials with long-term durability performance. The current project explores the development and use of a novel ductile, resilient composite material, improving the safety and resilience of civil infrastructures and reducing their repair and maintenance costs. For that purposes, nano boron nitride with two-dimensional layered structure has incorporated into sustainable engineered cementitious composites (ECC) to reinforce/modify their properties and performances. Then, flexural strength, compressive strength, and ultrasonic pulse velocity experiments were conducted on the prepared composites. One of the main objectives of this project is also to provide an in-depth understanding of the cracking characteristics and fracture behaviour of the samples in the light of micro-structural analysis obtained by using Scanning Electron Microscopy (SEM), X-Ray Diffraction method, and fractal theory. The investigation into the characteristics of these damages through systematic experimental and numerical analyses, will help better tailor and design nano modified engineered cementitious composites with desirable engineering properties, which would further promote the usage of this innovative composite in structural applications.

1 INTRODUCTION

Many buildings and infrastructure are made of concrete, but the brittle behaviour of concrete makes it more vulnerable. So, ECC are designed by Li, based on a micromechanical model providing ductility [1]. ECC is a class of ultra ductile fiber reinforced cementitious composites. ECC have approximately 500 times larger tensile strain capacity than that of normal concrete or fiber reinforced concrete (FRC) [2]. Based on prior research, ECC display a wide range of compressive strengths, from 20 MPa and 95 MPa. Suchlike, the tensile strengths of ECC vary from 4 MPa and 12 MPa. ECC are emblematized by 3% or more of strain capacity, by incorporating approximately 2 % polyvinyl alcohol (PVA) fibers [3,1]. The cracks in ECC can be controlled below 100 μm in width, which significantly improves the structural properties. The low crack width helps to ensure the self-healing behaviour of ECC. Also, this promotes the recovery of ECC mechanical properties and the reduction of permeability [4].

ECC can be cast (including self-compacting casting), extruded, or sprayed. The advantages of high ductility in the hardened state and easily processable in the fresh state make ECC impressive for different applications [2]. Whit its exceptional strain-hardening, durability, and strong resistance to strain, ECC exhibits remarkable properties, and endurance qualities [5]. Generally, ECC is made with cement, fly ash, silica sand, water, chemical additives and short fibers. The mechanical performance of ECC can be improved in different ways such as fiber type or hybrid additions [6]. Despite numerous advantages over conventional concrete, ECC still have some limitations. For instance, because of the lack of coarse particles, its elastic modulus is lower than that of traditional concrete [7]. It is important to recognise some limitations linked to the implementation of modern technology in ECC. In order to address the limitation in ECC, the usage of nanoparticles is proposed to improve the nanoscale properties of concrete [3]. Nano use in ECC composites has increased recently, so it is necessary to understand the effect of nanomaterials in ECC. Different nanomaterials such as nano-$CaCO_3$, carbon nanotubes, nanoscale graphene, nano-SiO_2, nano TiO_2 and nano Al_2O_3 have been discussed in previous studies [8]. The use of nanoparticles has proven to be effective in the modification of composites, even with use a little amount of these nanomaterials. Nanomaterials have demonstrated their ability to enhance the properties of the composites. The use of nanoparticles in the civil engineering has gained significant interest owing to their many advantages, including enhanced mechanical characteristics [3].

This study focuses on the development of high strength ECC incorporating nano boron nitride. For that purpose, nano boron nitride with two-dimensional layered structure has incorporated into sustainable engineered cementitious composites (ECC) for flexural strength, compressive strength, ultrasonic pulse velocity experiments and micro-structural analyses.

2 MATERIALS AND METHODS

Cement used in the study is defined as CEM I 42.5 N Portland cement. The specific gravity of the cement used is 3.06 and the specific gravity of the fly ash used is 2.1. The aggregate used in concrete production has a silica sand with a specific gravity of 2.6, an average grain size of 120 µm and a maximum grain size of 300 µm. The PVA fibers of 12 mm lengths with aspect ratio of 857 were utilised. To increase the workability of composite mixtures, highly water-reducing superplasticizer additive named MasterGlenium® ACE 450 was used as 1 % of the cement weight. Mixing ratios are given in Table 1.

Table 1: Mixing ratios of composite

Cement	Fly Ash	Silica Sand	Water	PVA
1	1.38	0.87	0.69	2 %

Nano boron nitride (NBN) was added to these mixtures at the rates of 1%, 2% and 3% of the cement weight, respectively. Thus, 4 different mixtures were determined, including the reference. The purity of the nano boron nitride used is 99.7% and its size is 790 nm.

Firstly, cement, fly ash and silica sand were mixed in a Hobart mixer at 100 rpm for 1 min. Then, water and super plasticizer were added and mixed at 150 rpm for 1 min. The mixing process continued at 300 rpm for another 2 min to achieve the uniform condition of fresh mortar. Afterwards, the fibers were added and the mixing process was run at 150 rpm for 3 min. Finally, nano boron nitride added and was mixed at 150 rpm for 2 min. The produced composites were 50 mm cubes for compressive strength tests and 350x50x15 mm prisms for 3-point bending tests. Three replicates have been produced for all the tests. After pouring and 24 h, the composites were stored in plastic bags to minimise moisture loss on the 28th day. The mixing process and prepared composites are shown in Figure 1.

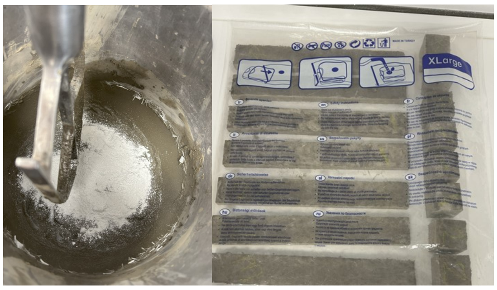

Figure 1: Mix process and the prepared ECC specimens.

As a non-destructive test, ultrasonic pulse velocity test (UPV) was performed on the specimens as per TS EN 12504-4 [9] to assess the quality of the composites (Figure 2). The travelling time between detectors was measured and the UPV was calculated.

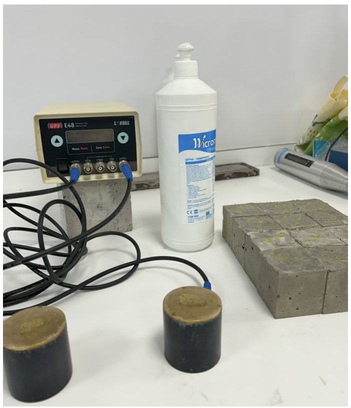

Figure 2: Ultrasonic pulse velocity measurement.

The compressive strength test was performed by applying pressure to the cube samples measuring 50 mm in Figure 3. Hydraulic press was used as the test instrument. In the compressive test, the loading speed was selected as 0.6 MPa/s in accordance with ASTM C39 [10].

Figure 3: Compressive strength test.

Flexural bending test was carried out on ECC specimens with dimensions of 350x50x15 mm prisms. The loading speed was 0.02 mm/s in accordance with ASTM C348 [11]. The composites were placed in the test device so that the distance between the supports was 300 mm in Figure 4. After the test, the flexural strength and displacement at the mid-span were taken from the device and stress-deformation curves were obtained. For each mixture, three specimens were measured and the mean values were adopted for analysis and discussion.

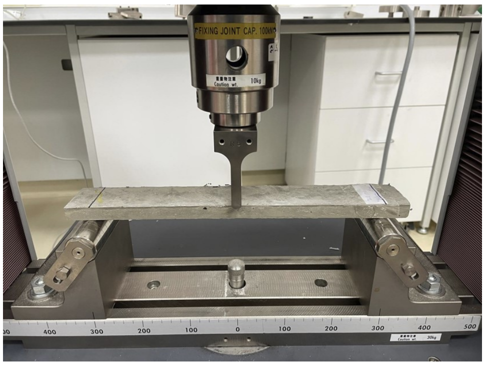

Figure 4: Flexural bending test.

Crack analysis was carried out after the bending test. Crack maps were created using Image J software from the surface crack photographs of the composites, and fractal dimensions are calculated with software. Fractal geometry concept is used to quantitatively describe the geometry of objects with irregular shapes such as crack. The fractal dimension has a value varying between 1 and 2 [12]. Fractal dimension values were calculated in the photographs of the surface cracks and estimated the energy emitted during crack propagation with the following formula:

$$W_s / G_f = h \cdot \left(\delta / h \right)^{1-D} \quad (1)$$

In Equation (1), h denotes the Euclidean length, δ indicates the maximum size of the silica sand and D indicates the fractal dimension of the crack.

The X-Ray Diffraction method (XRD) is based on the principle that each crystal phase refracts X-rays in a characteristic order depending on their atomic arrangement. For each crystal phase, these diffraction profiles define that crystal. With this analysis, it is possible to see phase changes in the crystalline structure [13]. Also, Scanning Electron Microscopy (SEM) was adopted to explore the microstructure of ECC matrix across the crack interface in ECC.

3 RESULTS AND DISCUSSION

3.1 Ultrasonic Pulse Velocity

When the ultrasonic pulse velocity values were compared with the reference mixture, they decreased by 2.1% with the addition of 1% NBN, 1.7% with the addition of 2% NBN, and 2.6% with the addition of 3% NBN in Figure 5. However, since all values were greater than 3.5 km/s despite the decrease, it can be interpreted that the internal structure of the composites was in good condition.

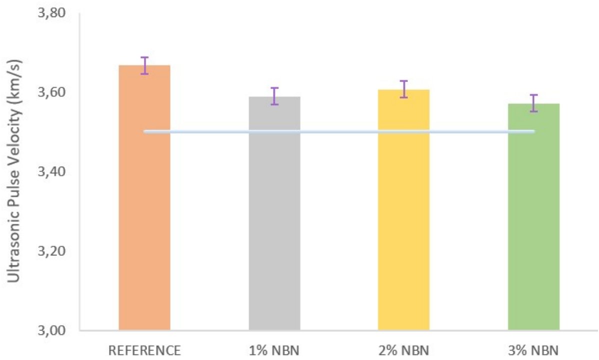

Figure 5: Ultrasonic pulse velocity results.

3.2 Compressive Strength

The compressive strength test results are given in Figure 6. Compared to the reference mixture, with the addition of 1%, 2% and 3% NBN, compressive strength decreased by 3.1 %, 8.6 %, and 9.3 %, respectively. This decrease in compressive strength can be explained by the formation of more voids in the internal structure as the NBN percentage increases. Internal structure images are shown in Figure 7. In addition, due to the high amount of fly ash, it is expected that the decreases in compressive strength will decrease in the long term. In the EDS analysis results in Figure 8, differences in atomic percentage distribution are seen in the composites with 3% NBN addition compared to the reference. The amount of boron is 12.2% elementally in the composite with 3% NBN addition.

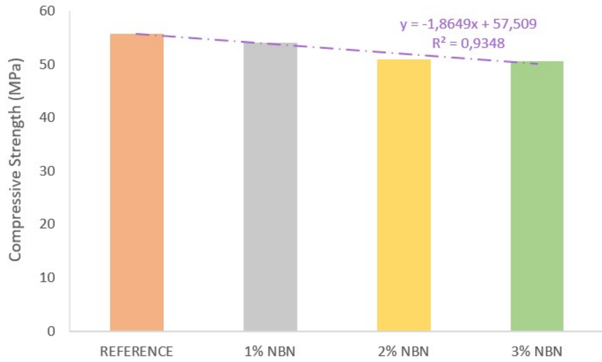

Figure 6: Compressive strength results.

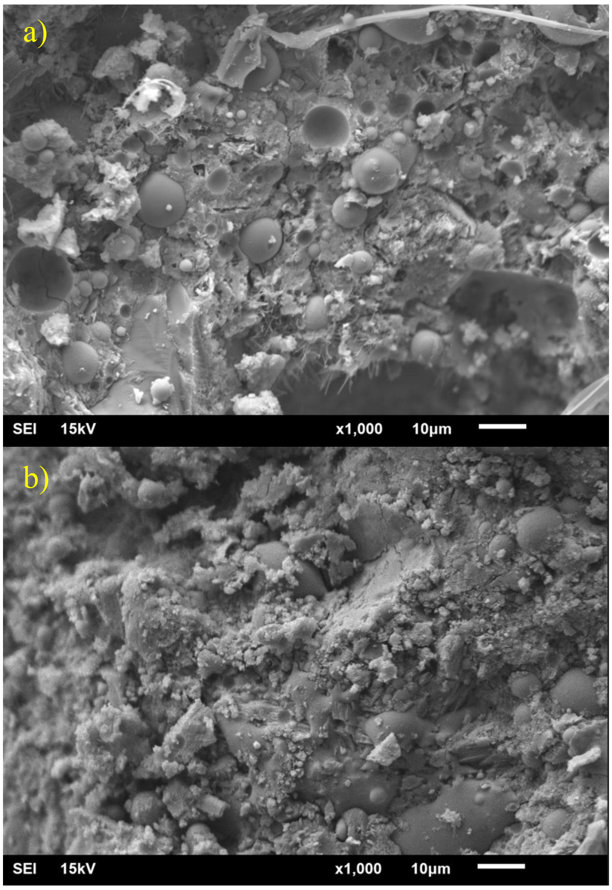

Figure 7: SEM images of ECC (a) reference, (b) 3% NBN added.

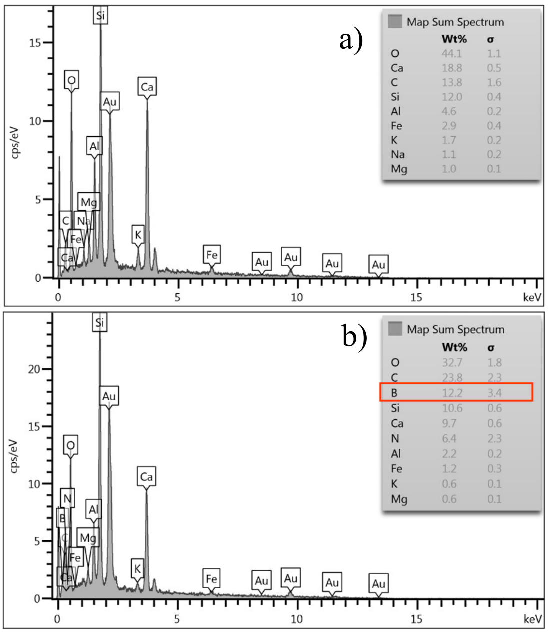

Figure 8: EDS analysis of of ECC (a) reference, (b) 3% NBN added.

3.3 Flexural Behaviour

The flexural stress-deformation curves of NBN-reinforced ECCs are seen in Figure 9. The flexural strength and mid-span displacement corresponding to the maximum bending load are summarized in Table 2 as the average of three specimens for each mixture. The highest flexural strength was obtained for 3% NBN added mixture as 13.81 MPa. Flexural strengths increased by 11,9 %, 34.1 % and 44 % with 1 % NBN, 2 % NBN, and 3 % NBN, respectively, when compared to the reference mixture. When the results are examined, it is seen that all beams exhibit deformation hardening and multiple crack behavior.

Table 2: Flexural strength and mid-span displacement results

	Flexural strength (MPa)	Mid-span displacement (mm)
Reference	9.59	2.25960
1% NBN	10.73	3.26111
2% NBN	12.86	3.55268
3% NBN	13.81	7.18038

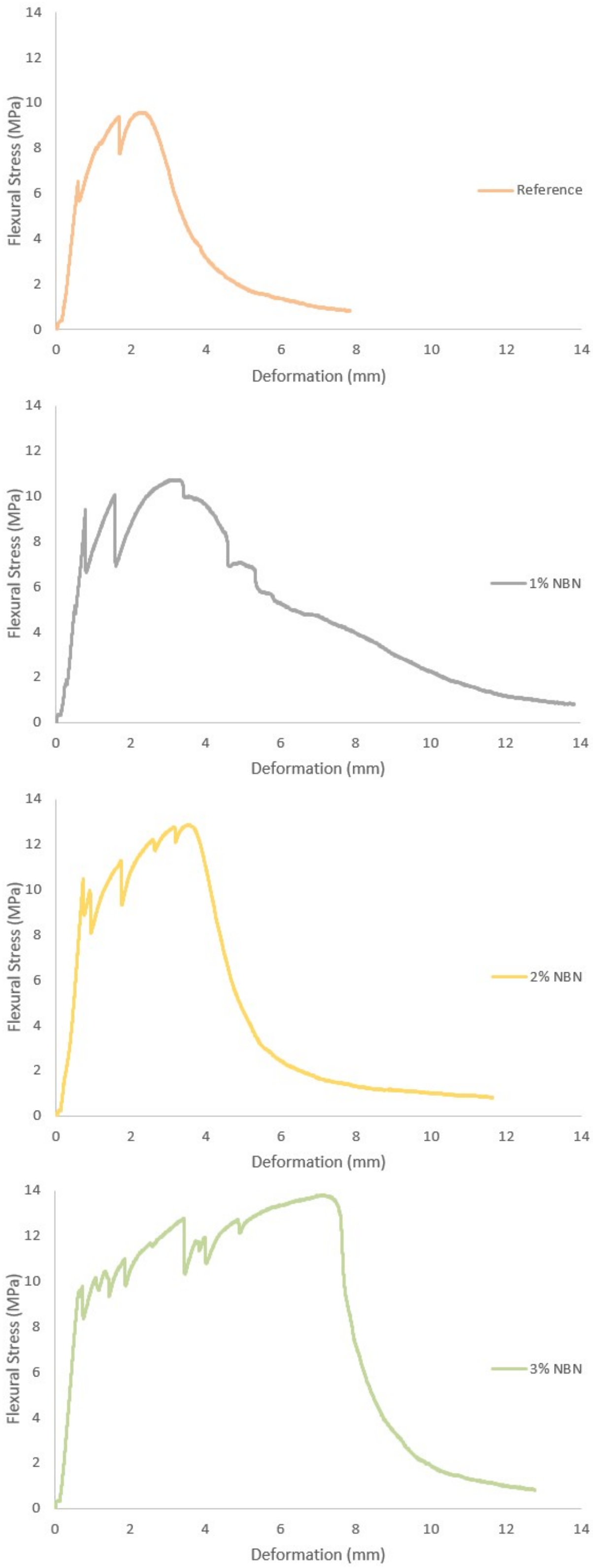

Figure 9: Flexural stress-deformation curves.

3.4 Fractal Analysis

Fractal analysis was performed from the surface cracks of the ECC. Fractal dimension values were obtained as seen in Figure 10. Also, the 3D images of crack damages obtained by analysis are seen in Figure 11. Fracture energy (Ws/Gf) values were calculated using fractal dimension values as seen Figure 12.

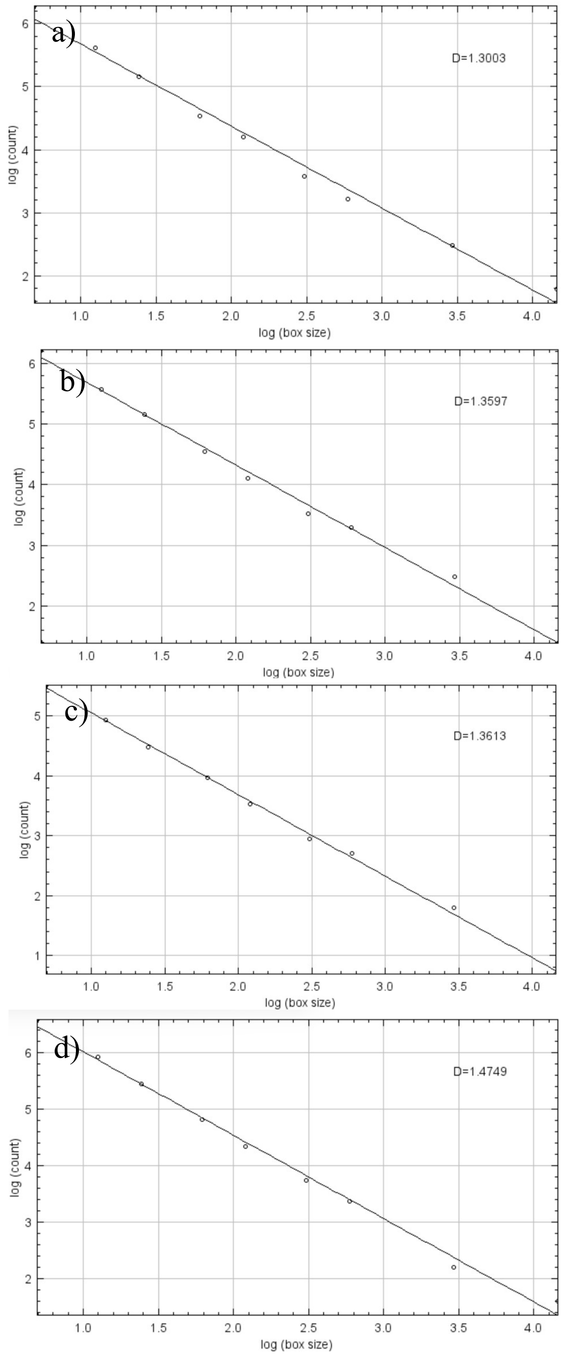

Figure 10: Fractal dimension values of (a) reference, (b) 1% NBN, (c) 2% NBN, and (d) 3% NBN.

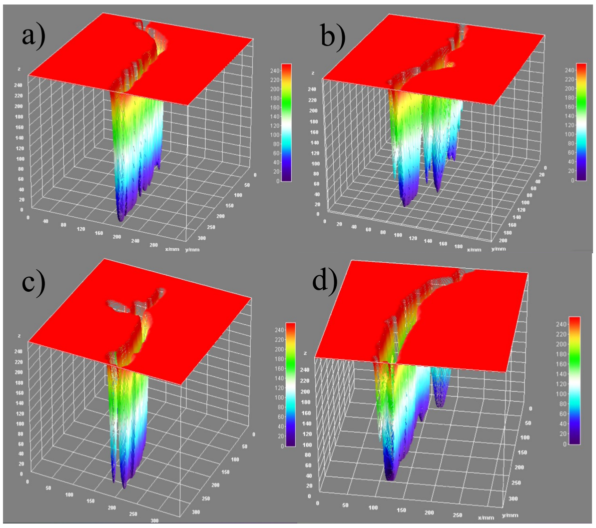

Figure 11: 3D images of crack damages of (a) reference, (b) 1% NBN, (c) 2% NBN, and (d) 3% NBN.

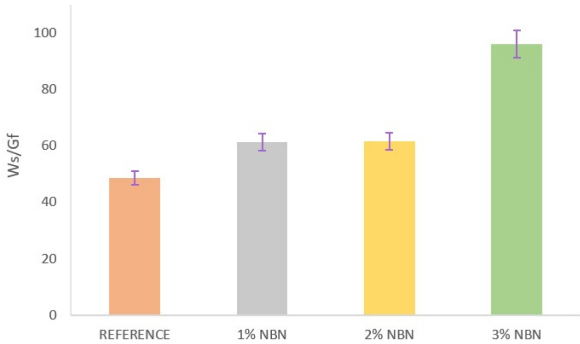

Figure 12: Fracture energy (Ws/Gf) values.

According to the fractal dimension and fracture energy data summarized in Table 3, compared to the reference mixture, with the addition of 1%, 2% and 3% NBN, the fracture energy increased by 26 %, 27 %, and 98 %, respectively. It is seen that the Ws/Gf value increases with the addition of NBN. Thus, the Ws/Gf results in ECC mixtures with NBN added can be interpreted as allowing the composites to have more energy absorption capacity.

Table 3: Fractal analysis and fracture energy results

	Fractal dimension	Ws/Gf
Reference	1,3003	48,6
1% NBN	1,3597	61,3
2% NBN	1,3613	61,6
3% NBN	1,4749	96,1

3.5 XRD Analysis

The XRD patterns of the reference and the boron nitride nano-particle reinforced sample with the best mechanical performance are illustrated in Figure 13. The patterns showed that there are only a few new peaks in the template, but the intensity of the peaks has significantly changed. Moreover, the boron nitride nano particle pattern would have amorphous content, most likely silica and thus, pozzolanic characteristics, as indicated by the hump in the diffraction pattern arrowed (Figure 13).

The pattern also confirmed that the addition of boron nitride nanoparticles to the mix has improved the peak intensity of the main hydration phases of portlandite and C–S–H gels which could be attributed to the acceleration of hydration process. This, in turn, produced a denser and strong structure associated with less porous and less cracks as confirmed by the SEM micrographs.

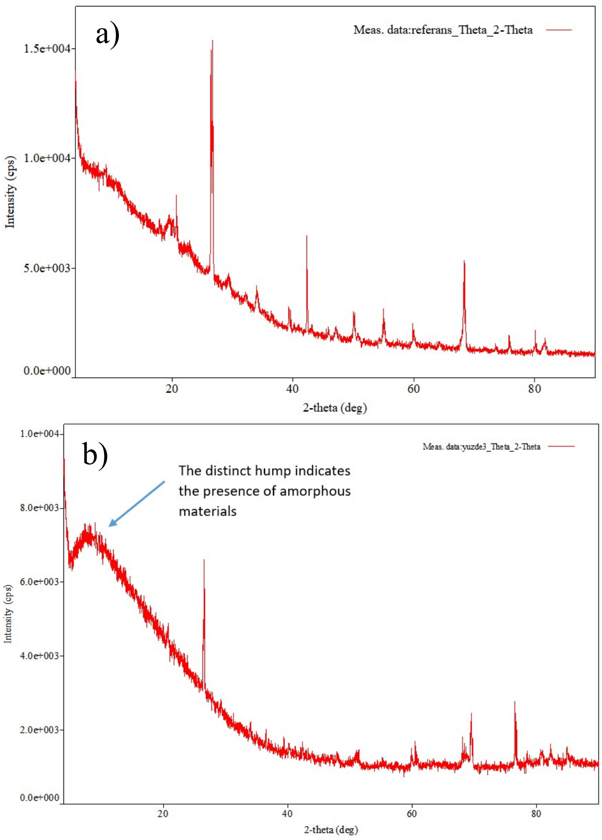

Figure 13: XRD analysis results of (a) reference and (b) 3% NBN.

4 CONCLUSIONS

In the presented study, ECC as a cement-based composite was produced using 3 different ratios of nano boron nitride, the mechanical properties and crack analyses of the produced composite were carried out. In the light of the obtained results:

- A slight decrease in compressive strength as the nano boron nitride additive ratio increases,
- Up to 44% increase in flexural strength depending on the nano boron nitride additive ratio,
- According to the crack analysis results, as the amount of nano boron nitride increases, the fracture energy increases.

In the light of the results obtained, nanoparticles as NBN can be used to improve the quality of cement-based materials. ECC is a promising material in terms of sustainability and innovation in materials contained and mechanical properties. For future research, a thorough mechanical, impact and durability study can be carried out with using nanoparticles.

ACKNOWLEDGEMENTS

The first author would like to acknowledge the TUBITAK 2224-A - Grant Program for Participation in Scientific Meetings Abroad for sponsoring this research.

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